

Hydrogenation of Vegetable Oils Using Mixtures of Supercritical Carbon Dioxide and Hydrogen

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ABSTRACT: Hydrogenation of vegetable oils under supercritical conditions can involve a homogeneous one-phase system, or alternatively two supercritical components in the presence of a condensed phase consisting of oil and a solid catalyst. The former operation is usually conducted in flow reactors while the latter mode is more amenable to stirred, batch-reactor technology. Although many advantages have been cited for the one-phase hydrogenation of oils or oleochemicals using supercritical carbon dioxide or propane, its ultimate productivity is limited by the oil solubility in the supercritical fluid phase as well as unconventional conditions that affect the hydrogenation. In this study, a dead-end reactor has been utilized in conjunction with a head-space consisting of either a binary fluid phase consisting of varying amounts of carbon dioxide mixed with hydrogen or neat hydrogen for comparison purposes. Reaction pressures up to 2000 psi and temperatures in the range of 120–140°C have been utilized with a conventional nickel catalyst to hydrogenate soybean oil. Depending on the chosen reaction conditions, a wide variety of end products can be produced having different iodine values, percentage *trans* fatty acid content, and dropping points or solid fat indices. Although addition of carbon dioxide to the fluid phase containing hydrogen retards the overall reaction rate in most of the studied cases, the majority of products have low *trans* fatty acid content, consistent with a nonselective mode of hydrogenation.

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KEY WORDS: Carbon dioxide, hydrogenation, reaction, supercritical fluid, vegetable oil.

Hydrogenation of vegetable oils is a traditional oleochemical modification process that has undergone limited change since its inception earlier in this century. Recently the concept of utilizing supercritical fluid conditions for improving hydrogenation of fats and oils has been advocated based on several criteria. These include improvement in mass transfer of the reactants to the surface of the catalyst particles, higher reaction rates, reduction in the amount of hydrogen required, and reduction of undesirable by-products yielding a higher end-product quality. Such results are a direct result of the use of supercritical fluids in hydrogenation processes which result in accelerating heat transfer, decreasing oil viscosity, and enhancement of hydrogen solubility in the oil phase.

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Several investigators have shown the efficacy of conducting hydrogenation of oleochemicals where both hydrogen and the fluid of choice (usually supercritical carbon dioxide, SC-CO₂) are technically in the supercritical fluid state. These studies have been predominantly carried out in tubular flow reactors by Harrod and coworkers (1–3) and Tacke *et al.* (4,5), and have utilized mostly nontraditional catalysts to accelerate the hydrogenation reaction. Recently, Andersson and King (6) expanded on these initial studies and successfully coupled a transesterification reaction conducted in SC-CO₂ with downstream supercritical hydrogenation to produce saturated fatty alcohols directly from vegetable oil feedstocks. A variation in using a batch reactor for the hydrogenation of hops (7) has been patented using either the addition of dry ice or liquid CO₂ to facilitate the synthesis of tetrahydroiso- α -acids. Likewise, Bertucco and coworkers (8) utilized an internal recycle reactor to hydrogenate unsaturated ketones.

Whereas conventional hydrogenation of vegetable oils is accomplished in a multiphase, gas–liquid system at low pressures in which the hydrogen is contacted with a nickel-based catalyst that is suspended in the vegetable oil, the above supercritical hydrogenation systems employ a one-phase system in which the oil is dissolved in the supercritical fluid at much higher pressures. In addition, traditional oil hydrogenation processes use batch-stirred autoclave reactors as opposed to fixed-bed flow reactors which are conveniently utilized with the above binary fluid mixtures. Such factors, coupled with supported palladium, platinum, or possibly ruthenium- or rhodium-based catalysts when used to demonstrate the benefits of conducting hydrogenation of vegetable oils in supercritical fluids, are in marked departure from existing industrial practice where supported, less expensive nickel catalysts yield a wide range of activity and selectivity.

The effect of pressure on the hydrogenation of vegetable oils has been studied by several research teams (9–12). It is found that in commercial dead-end reactors, dissolution of hydrogen in the oil is the rate-controlling step (13). Related to this study are the earlier efforts of Koritala and coworkers (11,12,14), who explored soybean oil hydrogenation at pressures up to 30,000 psi using nontraditional copper catalysts in both batch and flow reactors. Increasing pressure for the hydrogenation of vegetable oils is known to increase the reaction rate, the concentration of the hydrogen in the oil and on the catalyst surface, while negating selectivity and *trans*-isomer formation (15). A recent study by Fillion and Morsi

(13) has characterized the gas–liquid mass transfer and hydrodynamic parameters for the hydrogenation of soybean oil under industrial conditions. Generally, the above factors lead to a higher solids content in the resultant fat and higher, flatter solid fat indices (SFI) curves.

In this study the effect of using binary mixtures of SC-CO₂ and H₂ above the critical point of the mixture was tested using a standard industrial nickel catalyst in a batch, stirred reactor. The liquid phase consisting of oil, suspended catalyst, and dissolved binary fluid mixtures interfaced with a reactor headspace gas phase. The headspace gas phase varied in composition and applied pressure. Thus, the variation from a traditional hydrogenation practice (both selective and nonselective) is focused in changing the gas (fluid) phase while maintaining conventional reactor (stirred, batch) and nickel catalyst usage consistent with standard industrial practice. Additional benefits may also accrue when using binary fluid mixtures of CO₂ and H₂, such as the direct use of water gas shift reaction-derived CO₂ and H₂ mixtures without the need for prior gas-gas separation. Also the prophylactic effect of CO₂ addition to H₂ for increasing its flammability limit over that of neat H₂, as well as final product color improvement (16), provides extra incentives for considering the approach described in this study. For the above reasons, as well as reducing the departures from traditional processing methodology, it is hoped that the results obtained in this study might be considered for adoption by the oleochemical industry.

MATERIALS AND METHODS

Materials and analysis methods. A refined, bleached, and deodorized soybean oil (RBD-SBO) from Riceland Industries (Stuttgart, AR) that had an initial iodine value (IV) of 129 and a fatty acid composition of 18:0 = 4.2%, 18:1 = 23.1%, 18:2 = 52.5%, and 18:3 = 6.2% was used in all experiments. The extent of the hydrogenation reaction was monitored using an Abbe 3L refractometer from Bausch & Lomb (Rochester, NY) thermostated at 60°C. A plot of IV vs. refractive index (RI) was interpolated to measure the extent of the hydrogenation reaction.

Fatty acid compositions of the resultant products were determined by a standard procedure using gas chromatography and fatty acid methyl ester (GC-FAME) derivative formation (17). End products were also characterized by dropping point (D.P.) and SFI measurements as described in the *Official and Recommended Methods of the American Oil Chemists' Society* (18).

Hydrogen was obtained from BOC Gases (Murray Hill, NJ) and was 99.995% minimum purity grade. The CO₂ utilized in the experiments was also from BOC Gases and was of 99.8% minimum purity. Propane (Suburban Gas Company, Peoria, IL) was also briefly examined in place of CO₂ during the binary fluid hydrogenations. The nickel catalyst, Calsicat Ni catalyst droplets, E-479D, was obtained from Mallinckrodt Chemical, Inc. (Erie, PA). This consisted of 0.25 wt% nickel on the support. The catalyst charge to oil of 0.02 wt%

nickel concentration based on the weight of the oil was used in the hydrogenation experiment.

Hydrogenation reactors. The hydrogenation reactions, both conventional and with the aid of supercritical fluids, were performed using a standard Parr 2-L, batch autoclave (Parr Instruments, Inc., Moline, IL), equipped with both a pressure transducer and gauge for monitoring the pressure of the reactor. In-line with the above monitors was a relief valve in case of over-pressurization as well as a rupture disk for venting the contents of the reactor. The reactor also had type J and K thermocouples for measuring the temperature of the reactor. A vacuum exhaust line was used for venting the autoclave along with a gas/sampling inlet tube. Termination of the reaction as well as maintenance of the reactor's heat balance was aided by use of internal cooling coils. In addition, external air-cooling knives (Exair Corp., Cincinnati, OH) were used as an aid in cooling the reactor contents down after completion of the reaction.

Reaction parameters such as temperature, pressure, and agitation rate were monitored with the aid of a computer utilizing a National Instruments Inc. (Austin, TX) LabVIEW software program. As shown in Figure 1, an external Isco Model 260D syringe pump (Isco, Inc., Lincoln, NE) was used for pumping the hydrogen into the bottom of the reactor vessel to the required pressure and volume. Pressurized CO₂ was fed into the reactor by a Model AGT 162-52 gas booster pump made by Haskel, Inc. (Burbank, CA). To aid in establishing the pressure-based additions of the various gases, a second pressure transducer (PT), Heise Model ATS 2000 (Dresser Industries, Newtown, NH) was placed in-line between the delivery pumps and reactor vessel (see Fig. 1). External cooling water for the reactor was from an in-house, deionized water supply, triggered by a solenoid valve on demand, and the shaft of the reactor's mechanical stirrer cooled with the aid of a Neslab Instruments (model RTE-100, Portsmouth, NH) circulating water bath held at -15°C.

Reaction conditions. Conditions for establishing a baseline for conventional selective hydrogenation were: 170°C, 15 psi H₂, 0.05 wt% Ni catalyst, medium stirring rate (ca. 400 rpm). For nonselective hydrogenations, the conditions were: 120°C, 50 psi H₂, 0.02 wt% Ni catalyst, and high stirring (ca. 800 rpm). For these experiments, 950 g of RBD-SBO were used in the Parr reactor.

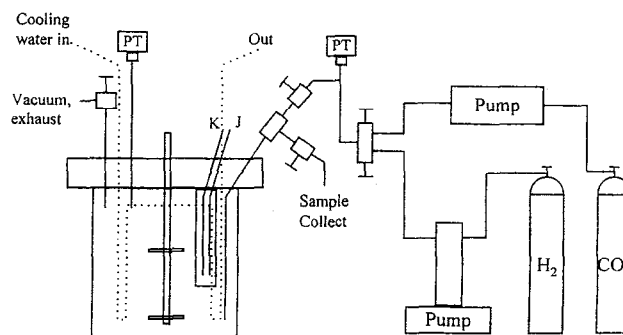


FIG. 1. High-pressure hydrogenation system for conducting conventional and binary hydrogenations on soybean oil (SBO). PT, pressure transducer; J and K, thermocouples.

Initially, supercritical reaction conditions using binary mixtures of CO_2/H_2 were as follows: 2000 psi CO_2 + 100 psi H_2 (2,100 psi total), 120°C, 0.02 wt% Ni catalyst. In this case, the headspace volume of the reactor varied between 1000 and 1,500 mL for charges of 500 to 950 g of oil. Some brief experiments were also run with a $\text{C}_3\text{H}_8/\text{H}_2$ system in which 1,000 or 1,400 psi of propane would be blended with 100 psi of H_2 . For the $\text{C}_3\text{H}_8/\text{H}_2$ system, reaction conditions were the same as for the CO_2/H_2 system above, except only 200 g of oil was utilized. These initial conditions for the CO_2/H_2 and $\text{C}_3\text{H}_8/\text{H}_2$ produced nonselective hydrogenation.

A variation in the respective amounts of the components in the binary fluid system, CO_2 and H_2 , was also made using the following conditions: 1,000 psi CO_2 + 1,000 psi H_2 , 500 psi CO_2 + 500 psi H_2 , and 250 psi CO_2 + 250 psi H_2 . All of these reactions were performed at 120°C using 0.02 wt% Ni catalyst, with high stirring in the reactor containing 500 g of oil.

Hydrogenation conditions using higher hydrogen pressures were as follows: 120°C, 0.02 wt% Ni catalyst, and 500 g of RBD-SBO. In this case, a pressure ladder of 500, 1,000, and 1,900 psi of H_2 was run using the above conditions. To observe the effect of increasing the reaction temperature to 140°C, two CO_2/H_2 systems were used with 2,000 psi CO_2 and 100 psi H_2 or 500 psi CO_2 and 500 psi H_2 , respectively. A reference hydrogenation was also run using only a 500 psi H_2 atmosphere. All of these reactions were conducted at 140°C, 0.02% Ni concentration, 800 rpm stirring rate, with 500 g of soybean oil.

A typical reaction sequence consisted of metering the gases (fluids) to the required pressures after heating the RBD-SBO to the desired reaction temperature under vacuum. When required, cooling water to the reactor coils was applied to counteract the effects of the hydrogenation exotherm. After the reaction was conducted for a specific time, the reactor was shut off and cooled to ca. 65°C, before venting the gases utilized in the experiment. Collected oil samples for characterization were filtered through celite.

RESULTS AND DISCUSSION

Initial supercritical reaction conditions. Initial reactions using either the specified CO_2/H_2 or $\text{C}_3\text{H}_8/\text{H}_2$ reaction condi-

tions produced no change in the IV of the product, even for reactions run 4–6 h. Therefore this approach was abandoned in favor of using binary fluid mixtures in which the CO_2 and hydrogen pressure were equivalent, utilizing nonselective hydrogenation conditions. In this case, equivalent gas pressures ranging from 250 to 1,000 psi were utilized.

Binary supercritical fluid mixtures. In Table 1 the hydrogenated oil products, using the above gas compositions, were characterized with respect to their IV, percentage *trans* fatty acid content, and overall fatty acid composition for 2- and 4-h reaction times. Also included in Table 1 are the results from conducting hydrogenation with just H_2 at 50 psi for the same time period. Here the extent of hydrogenation decreases as the overall pressure of the binary fluid system decreases as indicated in the corresponding IV values. The percentage of *trans* fatty acid content at either 2- or 4-h sampling periods also decreased as the overall system pressure was decreased (10), as did the saturated fatty acid content of the resultant oil (i.e., stearic acid). These two results suggest that nonselective hydrogenation is taking place under these conditions, yielding oils that have quite different properties from the nonselective hydrogenated product produced at 50 psi.

Pure H_2 elevated pressure hydrogenations. Additional hydrogenations were run without the second supercritical fluid component, i.e., SC- CO_2 , using a nearly equivalent total pressure to that used in the above-described CO_2/H_2 pressure ladder. These results are tabulated in Table 2 for 2- and 4-h sampling intervals so as to compare them against the nonselective, lower-pressure hydrogenation results. In this case, the IV of the resultant hydrogenated oils is similar to the IV exhibited by the product from nonselective low-pressure hydrogenation. The percentage of *trans* fatty acid content of the hydrogenated oils produced using higher hydrogen pressures is significantly lower compared to the oil hydrogenated at 50 psi, while the stearic acid content increased using a higher hydrogenation pressure. These results point to a set of reaction conditions that can produce low *trans* fatty acid levels, but that is inherently nonselective with respect to the mode of hydrogenation.

Effect of reaction temperature. Experiments were also conducted to see what effect the reaction temperature would have on the results of the hydrogenation (Table 3). In this case hy-

TABLE 1
Properties of Soybean Oil Hydrogenated Using Binary Fluid Mixtures of Carbon Dioxide and Hydrogen

Soybean oil (%)	Nonselective 50 psi H_2		1,000 psi CO_2 1,000 psi H_2		500 psi CO_2 500 psi H_2		250 psi CO_2 250 psi H_2	
	Time (h)		Time (h)		Time (h)		Time (h)	
	2	4	2	4	2	4	2	4
	IV ^a		IV ^a		IV ^a		IV ^a	
<i>Trans</i>	105	69	116	82	118	96	122	109
18:0	7.1	23.3	1.9	6.4	1.5	5.0	1.4	3.8
18:1	5.8	16.8	8.3	23.5	7.3	17.0	5.7	10.7
18:2	42.6	61.4	28.2	35.6	27.6	33.2	26.6	31.4
18:3	33.8	6.4	45.2	25.2	46.6	33.3	48.9	40.3
18:3	2.8	0	4.8	2.0	5.0	3.4	5.3	4.2

^aIV, iodine value.

TABLE 2
Properties of Hydrogenated Soybean Oils Produced Using Pure Hydrogen^a

Soybean oil (%)	Nonselective 50 psi H ₂		1,900 psi H ₂		1,000 psi H ₂		500 psi H ₂	
	Time (h)							
	2	4	2	4	2	4	2	4
	IV							
	105	69	108	75	108	72	110	76
<i>Trans</i>	7.1	23.3	2.7	7.0	3.1	7.4	3.4	8.6
18:0	5.8	16.8	11.7	27.8	12.6	30.8	11.0	26.9
18:1	43.6	61.4	29.2	35.3	29.1	33.0	29.7	35.7
18:2	33.8	6.4	41.2	21.7	40.9	21.2	41.5	22.2
18:3	2.8	0	3.5	1.3	3.6	1.8	4.3	1.9

^aSee Table 1 for abbreviation.

drogenations of soybean oil were performed with a binary fluid system of 500 psi for both CO₂ and H₂, as well as in pure H₂ at a 500 psi level, but the reaction temperature was 140°C, rather than 120°C. Here we observed a difference from the oil properties achieved previously when comparing the results from hydrogenating with a binary fluid mixture vs. pure hydrogen at 500 psi. In this case, both the IV and percentage of *trans* fatty acids, as well as the stearic and oleic acids contents are very close for the two above reactions.

Comparison of results between different reaction conditions. Figure 2 is a plot of reaction time vs. IV value for the hydrogenated soybean oil products. In Figure 2 the symbol codes have been grouped together: the first three representing hydrogenations conducted at elevated pressures in a pure hydrogen atmosphere, the next three representing the binary fluid mixtures at 120°C followed by a conventional low-pressure hydrogenation at 50 psi, and then hydrogenations done at 140°C. As noted by others (19), an increase in pressure increases the reaction rate for hydrogenation (steeper IV vs. time plots) for the CO₂/H₂ mixtures. Figure 2 leads one to the conclusion that the binary gas mixtures are retarding the hydrogenation reaction relative to pure H₂ at 120°C. The use of higher pressures with pure H₂ yields no apparent advantage above 500 psi in terms of reaction rate (10) and yields results similar to those obtained at 50 psi. Two of the hydrogenations conducted at 140°C (500 psi CO₂/500 psi H₂ and

500 psi H₂) show a rapid drop in IV with reaction time compared to hydrogenations conducted under the above-described conditions. This trend can be partially ascribed to the increase in reaction temperature (11) but requires that enough H₂ be available to contact with the catalyst/oil (note the result for the 2,000 psi CO₂/100 psi H₂ mixture).

Figure 3 shows the relationship between the percentage of *trans* fatty acid vs. IV value of the resultant soybean oil. In this case, the *trans* fatty acid content–IV relationship is linear and independent of reaction pressure as observed by others (9), the lone exception being the 2,000 psi CO₂/100 psi H₂ hydrogenation conducted at 140°C which mimics the conventional low-pressure hydrogenation at 50 psi. Thus, the binary fluid compositions and pure H₂ atmospheres at higher pressures yield lower *trans* fatty acid content having similar IV values when compared with the traditional low-pressure hydrogenation conditions. Also note that for most of the hydrogenations in Figure 3, the percentage *trans* fatty acid content is 30% lower than that usually found in a hydrogenated soybean oil with an IV value of 70 (20). Also note that reaction conditions which yield the lower *trans* fatty acid content at similar IV continue to head downward in Figure 3, suggesting that the *trans* fatty acid content will continue to remain low as the reactions proceed under the described conditions.

The percentage of stearic acid content vs. IV (Fig. 4) shows similar loci for all the reported reaction conditions ex-

TABLE 3
Properties of Soybean Oils Hydrogenated at a Higher Temperature (140°C)^a

Soybean oil (%)	Nonselective 50 psi H ₂ 120°C		2,000 psi CO ₂ 100 psi H ₂		500 psi CO ₂ 500 psi H ₂		500 psi H ₂	
	Time (h)							
	2	4	1	3	1	2	1	2
	IV							
	105	69	104	65	88	39	91	48
<i>Trans</i>	7.1	23.3	9.0	25.4	7.2	12.0	6.9	12.3
18:0	5.8	16.8	5.3	16.1	19.3	49.0	19.8	43.8
18:1	43.6	61.4	46.3	69.7	36.7	33.1	33.2	33.9
18:2	33.8	6.4	31.1	2.2	28.0	4.4	30.5	8.9
18:3	2.8	0	2.2	0.2	2.7	-0.3	2.9	0.6

^aSee Table 1 for abbreviation.

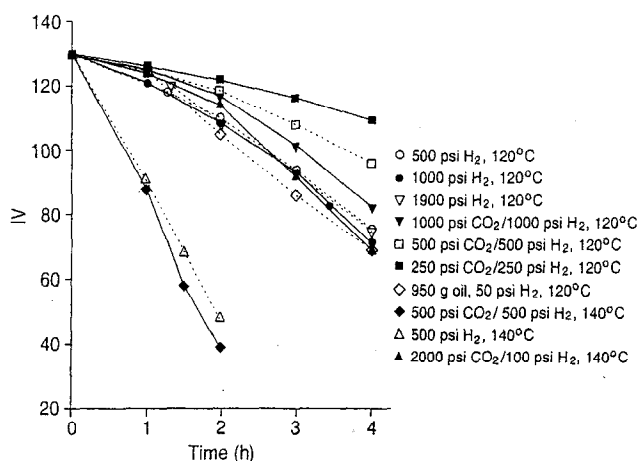


FIG. 2. Iodine value (IV) vs. reaction time for the hydrogenation of SBO under various experimental conditions. See Figure 1 for other abbreviations.

cept for the conventional low-pressure hydrogenation and the 2,000 psi CO₂/100 psi H₂ result at 140°C. These two hydrogenations yield a lower percentage of stearic acid in the final product that has a similar IV to that obtained under the other eight hydrogenation conditions. This corroborates the trends for *trans* fatty acid production shown in Figure 3 and indicates the nonselective nature of these hydrogenations.

Comparison of experimental products with commercial products. The results obtained from the described experimental hydrogenation runs have potential application in the food industry since the properties of the resultant oils closely approximate the IV, *trans* fatty acid content, and solid fat content (% 18:0) of margarine and shortening basestocks having similar D.P. A conventional margarine basestock will usually have a D.P. of 32–39°C and will exhibit the properties listed in Table 4. The hydrogenated oils obtained in this study have a slightly higher IV than that observed for a commercial mar-

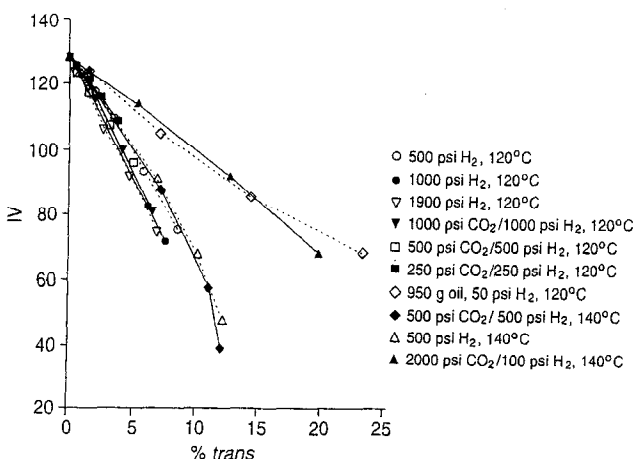


FIG. 3. IV vs. percentage of *trans* fatty acid (% *trans*) for SBO hydrogenated under various conditions. See Figures 1 and 2 for abbreviations.

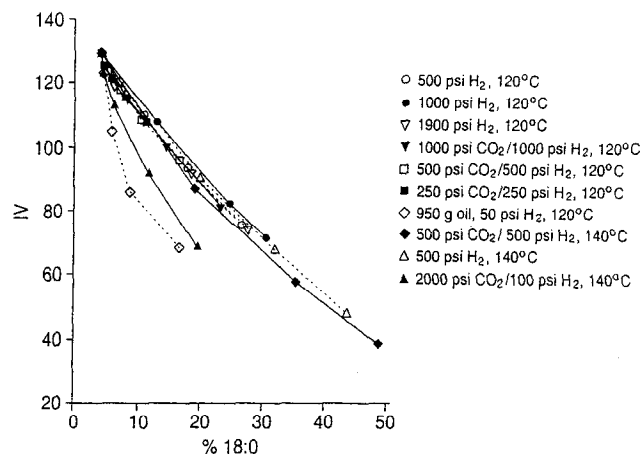


FIG. 4. IV vs. percentage of stearic acid (% 18:0) for SBO hydrogenated under various conditions. See Figures 1 and 2 for abbreviations.

garine basestock, the percentage of *trans* fatty acid being a decade lower than that found in a commercial sample. Table 4 also shows that the stearic acid content of both conventional margarine basestock and the hydrogenated oils is almost identical.

It is also possible to obtain a lower *trans* fatty acid content in the hydrogenated products compared to that found in a conventional shortening basestock (D.P. = 45–52°C) having a similar IV range (see Table 4). Table 4 also shows that our experimental hydrogenated products tend to have a slightly elevated level of stearic acid relative to levels found in commercial shortening basestocks.

Both of the above results suggest that the hydrogenation conditions described in this study offer considerable versatility in designing an appropriate basestock for margarine or shortening use. Particularly attractive is the lower *trans* fatty acid content relative to synthesized basestocks, since lower *trans* fatty acid levels in foodstuffs have an appeal to a health-conscious public (21,22).

SFI were measured for several of the hydrogenated oils synthesized in this study. Five of these products after 4 h of hydrogenation time were characterized by their SFI vs. temperature plots (Fig. 5). For the binary fluid mixtures and oil hydrogenated with pure H₂ at 1,900 psi, the temperature dependence of the SFI is a weak function of temperature. This

TABLE 4
Comparison of Experimental Hydrogenated Soybean Oils^a vs. Conventional Margarine and Shortening Basestocks

	Margarine basestock (D.P. 32–39°C)		Shortening basestock (D.P. 45–52°C)	
	Conventional	Experimental	Conventional	Experimental
%18:0	6–9	7–11	11–13	13–24
% <i>Trans</i>	11–30	1–3	15–20	3–8
IV	90–110	108–114	85–90	88–102

^aExperimental conditions: 120°C, 0.02 wt% Ni catalyst, 250 psi H₂, 250 psi CO₂. D.P. dropping point; see Table 1 for other abbreviations.

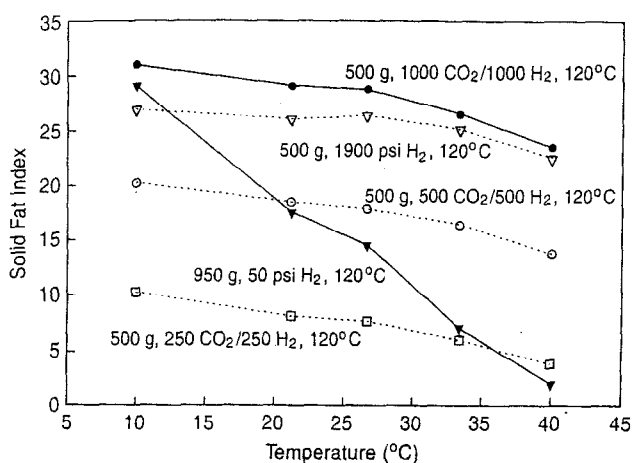


FIG. 5. Solid fat index (SFI) vs. temperature for five SBO hydrogenated using binary fluid mixtures (CO_2/H_2) and under conventional conditions. See Figure 1 for other abbreviation.

is similar to *trans*-suppressive hydrogenation, which yields a long plastic range of melting behavior desired for shortenings (23) but contrasts markedly with the SFI vs. temperature curve for the conventional hydrogenation conducted at 50 psi H_2 pressure. The SFI results in Figure 5 were all determined on hydrogenated oils having IV in the range of 60–70; however, the observed differences in their SFI vs. temperature curves reflect a varying saturated fatty acid content. For the four oils displaying an invariant SFI vs. temperature curve, it should be possible to stop the hydrogenation reaction earlier before the saturated fatty acid level increases to yield different SFI values.

The commercial utility of the products obtained by using the above hydrogenation methods is worth noting. Figure 6 illustrates the relationship between the percentage of *trans* fatty acid content of SBO hydrogenated at various conditions

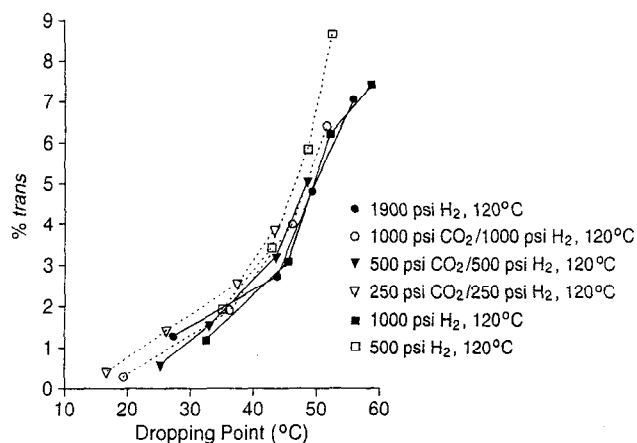


FIG. 6. Percentage of *trans* fatty acid content of SBO hydrogenated under various conditions with binary fluid mixtures (CO_2/H_2) and pure H_2 vs. dropping point of the resultant product. See Figure 1 for abbreviation.

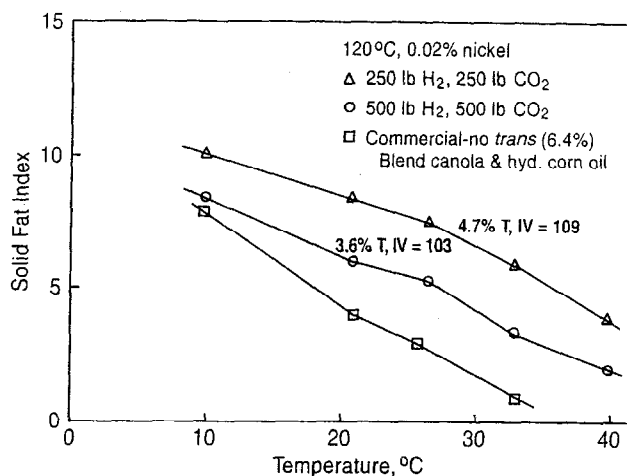


FIG. 7. Comparison of the SFI vs. temperature curves for potential low-*trans* shortening basestocks derived from binary fluid hydrogenations with low-*trans* fatty acid-blended oil mixture. % T, *trans* fatty acid content; hyd., hydrogenated. See Figure 2 for abbreviation.

along with their respective D.P. vs. temperature curves. For both the pure hydrogen and CO_2/H_2 mixtures, the curves for percentage of *trans* fatty acid vs. D.P. are very similar, an encouraging feature since these D.P. can be achieved on oils having a low-*trans* fatty acid content.

By adjustment of the hydrogenation conditions, it is also possible to produce an oil having a low-*trans* fatty acid content (% T) at higher IV that behaves similarly to blending oil mixtures [e.g., a low-*trans* (6.4%) mixture consisting of canola and hydrogenated corn oils]. Such a comparison is made in Figure 7 between two hydrogenated SBO products produced using binary fluid mixtures of CO_2 and H_2 at elevated pressures and the above-mentioned blend of oils. The two hydrogenated SBO exhibit somewhat similar SFI vs. temperature curves as does the oil blend, making them good substitutes for such margarine basestocks that have low-*trans* fatty acid content.

The studies reported using supercritical hydrogenation conditions are in contrast to the reported increases in reaction rate noted by other investigators using flow-reactor systems and precious-metal catalysts (24,25). Hydrogenations run at higher pressures were found to be nonselective with respect to their mechanism of reaction, but they also produced oils having low-*trans* fatty acid content. The dependence of the final oil properties on the hydrogenation conditions suggests some unique opportunities for optimizing reaction conditions to produce an array of products having different physical and chemical properties.

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